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Large Resonant Third-order Optical Nonlinearity of CdSe Nanocrystal Quantum Dots

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Abstract. Resonant third-order nonlinear optical susceptibility and hyperpolarizability of CdSe nanocrystal quantum dots were revealed to be $\sim 2.6\times10^{-20}$ – 2.7×10^{-19} m^2/V^2 and $\sim 2.2\times10^{-40}$ m^5/V^2 by using nanosecond degenerate four-wave mixing at 532 nm. The large nonlinearity of the CdSe nanocrystals is attributed to the resonant excitation and multiple nonlinear optical processes.

1. Introduction

Colloidal semiconductor nanocrystals have drawn significant attention because of their distinct roles in technical applications, which include their application as a laser power limiter, saturable absorber, optical switch, spacecraft crack indicator, gas sensor, biological labeling, light-emitting diodes, and solar cells. Strong blue-shift of optical bandgap with wide tunability and quantum confinement of electrons in the colloidal quantum dot boundary modifies the optical properties of semiconductor nanocrystals, including nonlinear optical susceptibility and hyperpolarizability. It allows us to customize them according to required applications. In recent years, colloidal semiconductor nanocrystals have attracted great interest for their large nonlinear optical properties with wide bandgap tunability, which differ remarkably from bulk crystals.

Both resonant and non-resonant optical nonlinearity of various materials have been investigated for many years. The processes leading to non-resonant nonlinearity are usually in relatively fast time scales, which are good candidates for optical switching and nonlinear transmission limiting applications. On the other hand, the processes causing resonant nonlinearity are usually in relatively slow time scales, which results in huge optical nonlinearity. Resonant nonlinear optical materials are widely utilized for Q-switching using a negative nonlinear absorption property, and for nonlinear transmission limiting using a positive nonlinear absorption property as well as a nonlinear refraction property or nonlinear phase changes. We discuss the basic understanding of reverse saturable absorption or positive nonlinearity with resonance excitation, considering a multi-level system interacting with the optical field in semiconductor nanocrystals. The process of absorption in a multi-level system is as follows: Absorption of the incident field promotes electrons to the first or higher

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excited state dependent upon excitation wavelength. From the excited state the electrons can rapidly make a transition to an intermediate state by a non-radiative transition. Before the electrons are completely relaxed to the ground state, they may experience absorption that promotes them to a higher energy state. This process is called two-step absorption. When the absorption cross-section of the excited state is larger than that of the ground state, then the system will exhibit reverse saturable absorption phenomena or positive nonlinear absorption. Of course, it is saturable absorption if the cross-section of the excited state is smaller than that of the ground state.

In this paper, we present the resonant nonlinear optical properties of CdSe nanocrystals using degenerate four-wave mixing (DFWM) by a nanosecond laser pulse at 532 nm (Continuum, Powerlite, Nd:YAG laser, 8 ns, 10Hz).

2. Linear Optical Properties

The typical linear absorption spectra of TOPO- passivated CdSe in toluene are shown in figure 1. The absorption spectra of semiconductor nanocrystals with sizes near the exciton Bohr radius clearly exhibit discrete features because of transitions coupling electron and hole quantized states. The semiconductor nanocrystals also exhibit a strong blue-shift of bandgap energy because of their quantum confinement. The average diameter of CdSe nanocrystals was ~3.5 nm. Exciton absorption peaks of CdSe nanocrystals were ~565, 537, 469 and 405 nm. Absorption coefficients ($\alpha = 2.3A/d,\ d = 1\ cm$) at 532 nm were 3.5, 1.5, 0.76, and 0.35 cm^{-1} for different concentrations, where the value of absorbance *A* is given in the figure 1 and *d* is the sample length.

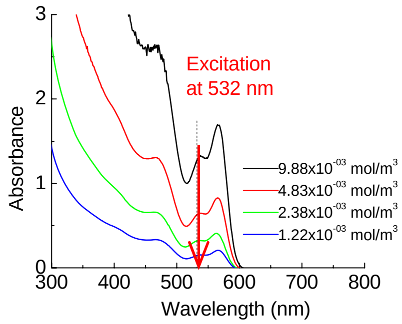

Fig. 1. Absorption spectra of CdSe nanocrystals in toluene. Average diameter of CdSe nanocrystals was ~3.5 nm, Exciton absorption peaks were ~565, 537, 469 and 405 nm.

The linear refractive index of CdSe nanocrystals was calculated to be ~2.34 for ~3.5 nm average diameter [1]

$$n_{CdSe} = \sqrt{1 + \frac{(\varepsilon_{bulk} - 1)}{1 + \left(\frac{0.75}{D}\right)^{1.2}}}\,, \tag{1}$$

where, ε_{bulk} ~ 6.2 is the dielectric constant of bulk CdSe, and D is the average diameter of CdSe quantum dots in nm.

3. Nonlinear Optical Properties

Figure 2 shows logarithmic plots of the DFWM signal from CdSe nanocrystals with resonance excitation of 532 nm and 8-ns temporal pulse width as function of total pump intensity at around zero delay. The DFWM signal near the zero delay was observed to be $I^{2.9\sim3.1}$, which indicates the dominance of the third-order nonlinearity at the irradiances near and less than 100 MW/cm^2.

The third-order nonlinear susceptibilities of samples (CdSe dots in toluene or toluene itself) were estimated using the following equation by comparison of the FWM signal beams of samples with that of CS_2 measured under identical conditions [2]

$$\chi_S^{(3)} = \sqrt{\frac{I_S}{I_R}}\left(\frac{n_S}{n_R}\right)^2\left(\frac{L_R}{L_S}\right)\left(\frac{\alpha L}{e^{-\alpha L/2}\left(1-e^{-\alpha L}\right)}\right)\chi_R^{(3)} \tag{2}$$

where I is the intensity of the FWM signal beam, n is the refractive index ($n_s(CdSe)$: given by equation (1), $n_R(CS_2)\sim 1.63$ [3]), L ($L_s=L_R=1\ mm$) is the sample path length in DFWM, α is the linear absorption coefficient (cm^{-1}) of the sample at 532 nm, and S and R indicate sample and reference. The excellent and stable third-order optical response solvent, carbon disulfide (CS_2, 99+ %, spectrophotometric grade, Aldrich), was selected as a reference. It has been assumed that the reference has no linear absorption at the excitation wavelength at 532 nm. The absorption length of CdSe in toluene for the DFWM experiment was αL ~ 0.35, 0.15, 0.076, and 0.035 << 1 for each of the four different concentrations as listed in the figure 1. Therefore, equation (2) is appropriate to calculate the third-order nonlinearity for the Kerr-like medium.

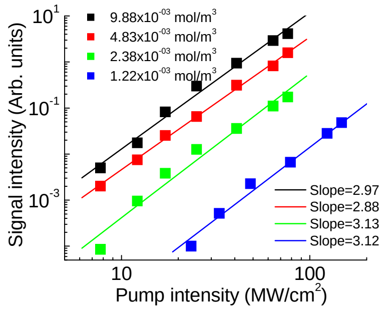

Fig. 2. Logarithmic plot of the DFWM signal in CdSe nanocrystals at 532 nm as function of total pump intensity at around zero delay. The solid line is a best fit to the data, giving an $I^{2.9\sim3.1}$ dependence.

The total third-order nonlinear susceptibility of the dilute sample of dots in a matrix (dot volume fraction<<1) is $\chi_{tot}^{(3)} = \chi_{dot\_eff}^{(3)} + \chi_{toluene}^{(3)}$, where, $\chi_{tot}^{(3)}$ and $\chi_{toluene}^{(3)}$ are the third-order nonlinear susceptibilities of the sample (dots in matrix) and toluene, and $\chi_{dot\_eff}^{(3)}$ is the effective third-order nonlinear susceptibility of CdSe quantum dots. The effective third-order nonlinear susceptibility $\chi_{dot\_eff}^{(3)}$ includes the dielectric effect of nanocrystals and toluene. The third-order susceptibility of pure toluene was measured to be ~1.6×10^{-21} m^2/V^2 (1.1×10^{-13} esu) comparing with the reference sample CS_2. The third order nonlinear susceptibility and the linear refractive index of CS_2 were reported to be ~9.5×10^{-21} m^2/V^2 (~6.8×10^{-13} esu) and ~1.63 at 532 nm in nanosecond time-scale [4]. Therefore, the effective third-order nonlinear susceptibilities of semiconductor nanocrystals were ~2.6×10^{-20} – 2.7×10^{-19} m^2/V^2 (~1.9×10^{-12} – 1.9×10^{-11} esu) for various concentrations of quantum dots 1.2×10^{-6} – 9.9×10^{-3} mol/m^3 in toluene.

The effective third-order nonlinear susceptibility of the CdSe nanocrystals is correlated with the dot concentration and the effect of the dielectric confinement [5]

$$\chi_{dot\_eff}^{(3)} = f^4 N_a \gamma^h C \quad (SI), \tag{3}$$

where $f = \dfrac{3n_{toluene}^2}{n_{dot}^2 + 2n_{toluene}^2}$ is the local field factor, n is the refractive index ($n_{dot}=n_s$: given by equation (1), $n_{toluene}\sim 1.5$ [2]), N_a is Avogadro's number, and C is the concentration of CdSe quantum dots. The second-order hyperpolarizability (γ^h) of CdSe nanocrystals were extrapolated from the slope $(f^4 N_a \gamma^h)$ of the third-order nonlinear susceptibility as a function of the concentration plot as shown in figure 3. The hyperpolarizability of CdSe nanocrystals was estimated to be ~2.2×10^{-40} m^5/V^2 (~1.6×10^{-26} esu). The unit conversion between $\chi^{(3)}$ and γ^h was made based on the following relationships [6]:

$$\chi^{(3)}\left[\frac{m^2}{V^2}, SI\right] = \frac{4\pi\times10^{-8}}{9}\chi^{(3)}[esu], \text{ and } \gamma^h\left[\frac{m^5}{V^2}, SI\right] = \frac{4\pi\times10^{-14}}{9}\gamma^h[esu]. \qquad (4)$$

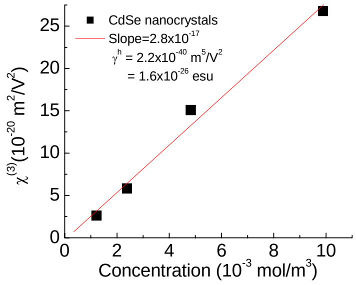

Fig. 3. Third-order nonlinear susceptibility as a function of the concentration of CdSe nanocrystals. The slope of linear fitting revealed the hyperpolarizability of CdSe nanocrystals.

The large nonlinearity of CdSe nanocrystals comes from the resonance excitation at 532 nm. It is well known that resonant excitation enhances the third-order nonlinearity significantly since many processes, such as electronic processes, nuclear processes, and even thermal processes, may contribute to the optical nonlinearity significantly. The possible thermal effect under long pulse laser irradiation is a disadvantage for photonic device applications. We are currently measuring the different components of the third-order nonlinear susceptibility tensor using polarization-resolved as well as time-resolved four-wave mixing techniques, which will help to identify the physical mechanism of the optical nonlinearity of the CdSe nanocrystals in resonant wavelength range.

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